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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

A/ft^2	ampere per square foot	kW•h	kilowatt hour
A•h	ampere hour	L	liter
°C	degree Celsius	lb	pound
g	gram	lb/yr	pound per year
g/(A•h)	gram per ampere hour	min	minute
g/L	gram per liter	mL	milliliter
h	hour	pct	percent
in	inch	V	volt
kg	kilogram	vol pct	volume percent
kV•A	kilovolt ampere	wt pct	weight percent

EXPERIMENTAL NICKEL-COBALT RECOVERY FROM MELT-REFINED SUPERALLOY SCRAP ANODES

By J. L. Holman[1] and L. A. Neumeier[2]

ABSTRACT

The Bureau of Mines is conducting research to recover strategic and critical metals such as Ni, Co, and Cr from mixed contaminated superalloy scrap. One approach being studied involves melt refining of superalloy scrap to produce anodes for electrolytic deposition of Ni-Co alloy. This melt refining of superalloy turnings is described based on melt-oxidation and oxidation-carburization experiments, using roasted superalloy grinding sludge to supply the O needed to oxidize Cr and other readily oxidized elements to the slag. Controlled melt-carburization subsequent to oxidation improved the metal phase recovery of Ni and Co to well over 90 pct and decreased electrolytic solubility of Cr, Mo, and W by carbide formation. Electrolytic refining experiments were conducted using a controlled-potential mode (preset cathode potential). Data show effects of Fe and Cr impurities, cation concentration, electrolyte pH, SO_4-Cl electrolyte ratio, temperature, cathode potential, and cation-selective membrane use on current efficiency, current density, and deposit composition. Disposition of Ni, Co, Cr, Mo, W, and Fe is compared for melt-oxidized versus oxidized-plus-carburized anodes. Deposits containing >97 pct Ni + Co (major impurity Fe) have been routinely obtained from scrap anodes. Research is continuing to improve deposit quality in sustained deposition and to recover Cr and other metals from refining slags and anode sludges.

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INTRODUCTION

The United States is highly reliant on foreign sources for its primary supply of Cr, Co, Ni, and other strategic and critical metals. To help decrease this foreign reliance, the Bureau of Mines is developing improved technology to increase the recycling of mixed contaminated Cr-Co-Ni-bearing scrap and waste materials. According to a Bureau-sponsored study of critical metals availability (1),[3] approximately 125 million lb/yr of mixed contaminated superalloy and associated heat- and corrosion-resistant high-alloy scrap is downgraded or exported. Even though Co usage has dropped in recent years, appreciable amounts of mixed scrap continue to be generated by turbine engine producers and other specialty fabricators. Superalloys comprise the largest single use category for Co. Because of stringent specifications for superalloys, little scrap is charged to these melts. Because of this, mixed contaminated superalloy-type scrap is commonly reprocessed by secondary metal refiners and downgraded in use as Ni-enriched feedstock for stainless steel, cast iron, or alloy steel.

Previous Bureau-developed recovery schemes for processing Ni- and Co-base scrap have had only limited application. These include Kenworthy's research that demonstrated removal of Cr from superalloy scrap (2) and Kusik's research on melt-oxidation of stainless steel scrap for subsequent reduction to ferrochromium (3). The research of deBarbadillo led to a procedure (4) whereby superalloy scrap was oxidized and sulfidized under controlled conditions. Beneficiated Cr sulfide was roasted and reduced aluminothermically, and Co and Ni sulfides were leached, solvent-extracted, and electrowon individually. Bureau research on superalloy reclamation in the 1960's used a variety of constant-current electrodeposition and hydrometallurgy techniques (5-6).

The current investigation includes melting scrap charges, refining the melt, and casting soluble anodes for electrorefining a recyclable Ni-Co alloy. This combined pyrometallurgical and electrometallurgical approach utilizes controlled-potential electrolysis to selectively deposit Ni-Co alloy. Electrolytic cells normally operate at constant current. In theory, controlled potential can deposit or reject elements depending on their respective standard reduction potentials.

An initial report of this research (7) described results from basic controlled-potential electrolysis studies performed on synthetic alloy anodes cast from elemental Ni, Co, and Cr. This report covers the melt refining of superalloy scrap anodes, the effects of Fe and Cr on the deposition of Ni-Co alloy, and the general techniques used to recover electrodeposited Ni-Co master alloy from superalloy scrap and grinding sludge. Ongoing work is directed toward improving deposit quality in sustained cell operation and assessing viable methods for recovering the Cr, Mo, and W partitioned to the refining slag or reporting as anode sludge in this research.

MATERIALS AND EQUIPMENT

Mixed contaminated superalloy (SA) turning scrap (deoiled) and oily contaminated SA grinding sludge generated by an aircraft turbine engine manufacturer were used in the experiments. Analyses of the as-received materials are given in table 1.

The melting of the scrap and melt refining experiments, consisting of melt-oxidation and melt-oxidation-plus-carburization treatments to partition Cr to the slag phase and Ni and Co to the metal phase, were conducted in a 10-lb-capacity, 17-kV·A indirect-arc electric rocking furnace (fig. 1). Slagging additions of lime, silica, and CaF_2 were made to the melts. The furnace had a high-alumina rammed lining. Melt temperatures

[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Compositions of as-received superalloy scrap turnings and grinding sludge, weight percent

	Turnings	Sludge[1]
Ni	54.1	24.2
Co	12.7	11.6
Cr	19.2	8.0
Fe	6.5	2.5
Mo	4.2	1.1
W	.7	3.5
Al_2O_3	NAp	30

NAp Not applicable.
[1]Contained about 10 wt pct oil.

were measured using disposable-tipped Pt versus Pt-13 pct Rh thermocouples and optical pyrometers. Heats were poured into refractory-washed conical carbon molds which had been preheated to 350° C. Selected metal products were remelted in a vacuum induction furnace under a partial He pressure and cast into anodes (1.50 by 6 by 0.25 in) in preheated mild steel book molds coated with a ZrO_2 slurry. In industrial practice, such melt refining and anode casting would, of course, be from one furnace without remelting.

Superalloy grinding sludge was roasted in air in a resistance-heated muffle furnace having an exhaust system attached to the door.

Electrolytic experiments were conducted in a 1- or 2-L glass cell (fig. 2) at an electrolyte volume of 900 or 1,400 mL. The cell temperature was maintained at

FIGURE 1.—Tapping a superalloy scrap heat from small arc furnace after oxidizing contained Cr to the slag.

FIGURE 2.—Electrolytic cell utilized in controlled-potential electrolysis experiments to deposit Ni-Co alloy from superalloy scrap anode.

55°±1° C, unless otherwise noted, with a constant-temperature circulating bath. This temperature was chosen based on work reported by Hayashi (5). The apparatus was described in a previous report (7).

The electrolytic cell was operated in a controlled-potential mode. To do this, a standard calomel electrode with a Luggin capillary tip near the cathode was connected through a potentiostat so that the cathode potential was controlled throughout the electrolysis at a predetermined value. The controlled-potential mode has the advantage with multielement systems of maintaining relatively constant deposition potential selected to be more negative than the effective threshold deposition potential for Ni-Co alloys. Coincidently, deposition or associated reduction reactions of elements, such as Cr, that have more negative deposition potentials (less noble) are restricted. The reduction potential for Ni-Co deposition is shifted from the ideal behavior of standard reduction potentials (table 2) for Ni and Co alone, as was expected, primarily because of polarization.

The electrolyte system chosen is acidic sulfate-chloride. This system was selected because of its ability to dissolve highly corrosion-resistant SA scrap anodes. The experiments have shown that

overall anode dissolution rates, particularly with substantial chloride present, consistently exceed deposition rates. That is, anode dissolution rate is not a limiting factor.

A cation-selective membrane (CSM), Nafion 425,[4] was used to separate the anolyte and catholyte chambers in most experiments to help control migration of impurities that tend to codeposit with Ni-Co alloy.

Metallic elements in SA scrap, melt-refined products, electrolyte samples, and cathode deposits were analyzed primarily using an inductively coupled plasma (ICP) spectrophotometer. Carbon, oxygen, and sulfur were determined by the combustion method. Standard gravimetric procedures were used to analyze for sulfate and chloride.

TABLE 2. - Standard reduction potentials of selected elements in superalloy scrap

Reduction reaction	Standard potential, V
$WO_2 + 4H^+ + 4e = W + 2H_2O$..	-0.12
$Mo^{3+} + 3e = Mo$.....	-.20
$Ni^{2+} + 2e = Ni$.....	-.25
$Co^{2+} + 2e = Co$.....	-.277
$Fe^{2+} + 2e = Fe$.....	-.44
$Cr^{3+} + 3e = Cr$.....	-.744

EXPERIMENTAL RESULTS AND DISCUSSION

PYROMETALLURGICAL ANODE PREPARATION

Melt-Oxidation

Previous research by Kenworthy (2) showed that Cr and other reactive metals in SA scrap melts could be selectively oxidized to the slag using NiO additions to molten superalloy. It also has been demonstrated (3) that molten SA heats can be blown with O or mixtures of air and O to selectively oxidize Cr and other reactive metals.

A modification of those melt-oxidation procedures was used to partition Cr, W, and some Mo to the slag phase during melting of SA scrap. The modified procedure utilized a waste material, SA grinding sludge, which also contained essentially the same critical metals as the turning scrap (table 1), although in different proportions. The SA grinding sludge (oily) was given a controlled oxidation roast at 1,050° C for 1 to 2 h to remove the oil and oxidize Cr, Ni, Co, Fe, and other elements. The oxidized sludge was then used as a charge ingredient in SA scrap melts to supply the bulk of the oxygen needed (from reducible Ni, Co, and Fe oxides) for partitioning oxidized Cr to the slag as Cr_2O_3 radical. The 30 pct alumina in the roasted SA sludge floats to the slag during the melt-refining treatments.

A series of heats was made in which the additions of roasted SA sludge were varied from 250 to 1,000 g per 500-g charge of SA scrap turnings, representing approximately 40 to 150 pct of the stoichiometric O calculated as needed to oxidize the Cr in the turnings (sludge Cr oxidized in roast). An oxidation period of 30 min was used after the melt was heated to 1,600° C. This resulted in a decrease in Cr content of the combined metal-bearing charge from about 12 to 15 pct (depending on sludge proportion) to the range of 4.6 pct to <0.01 pct with increased oxidized sludge additions.

After a number of oxidation tests had been made, it was evident that an addition of 882 g of roasted SA sludge (135 pct stoichiometric O) was suitable to reach <0.1 pct Cr in the metal phase after a 30-min oxidation period. An additional series of oxidation melts was made using 882-g sludge additions while varying the oxidation period from 5 to 60 min. The metal product contained 1.93 to <0.01 pct Cr (table 3). This series verified that a 30-min oxidation period was adequate for the oxidation to proceed essentially to completion.

[4]Reference to specific products does not imply endorsement by the Bureau of Mines.

TABLE 3. - Cr in melt-oxidation product relative to oxidation period with 135 pct stoichiometric O addition as roasted sludge

Oxidation period, min	Cr in metal, wt pct
5	1.93
15	.42
30	.02
60	.01

Although melt-oxidation can decrease the Cr content of the metal phase to a low level, other factors must be considered, such as the effects on the primary elements Ni and Co. Thirty-minute oxidation tests with 882 g roasted sludge per 500 g SA scrap chips have shown that approximately 35 pct of the Co and 15 pct of the Ni were oxidized to the slag. Some 90 pct or more of the W, ~50 pct of the Mo, and ~75 pct of the Fe also were oxidized to the slag. The loss of this much Ni and Co is undesirable for an efficient recycling process. Therefore, alternate processing methods were assessed to improve the Ni and Co recovery while retaining as much Cr as possible in the slag.

Melt-Oxidation-Carburization

One alternate method showing promise is melt-carburization (partial reduction) with C (as coke breeze, 78 pct C) subsequent to a 30-min melt-oxidation period, to reduce most of the oxidized Ni and Co back into the metal phase without causing excessive reduction of the Cr. This method worked to the extent that ~95 pct of the Ni and Co could be recovered in the metal phase, while ~85 pct of the Cr remained with the slag. Coincidently, about 75 pct of the Fe, 95 pct of the Mo, and 80 pct of the W reported in the metal phase. An added benefit resulting from the carburization was the formation of appreciable quantities of the Cr, Mo, and W as insoluble carbides that remained as anode sludge during electrolysis.

A number of melt-oxidation-carburization experiments were made. Most involved first oxidizing the melt for 30 min at 1,600° C using 135 pct stoichiometric O addition from roasted sludge as previously described, followed by stirring in varied amounts of coke breeze for 15 min before tapping into a conical C mold. The experiments showed that an addition of ~10 pct coke breeze (78 pct C) was sufficient to reduce well over 90 pct of the Ni and Co to the metal phase. This C addition represented some 300 pct of the C calculated as needed to reduce the oxidized Ni, Co, and Fe. As for the melt-oxidation heats, the slag and metal were separated upon solidification. The slags were crushed and run through a magnetic separator to remove any metal fines, which were added to the ingots for remelting of anodes. The minimizing of metal entrapment in the slag by forming more fluid slag and using a slow cooling rate is under investigation. Table 4 compares the distribution of elements between the slag and metal phases for oxidation-plus-carburization conditions of 135 pct stoichiometric O and 300 pct stoichiometric C addition with melt data for oxidation with the same O addition without carburization. The Ni and Co metal recoveries were well above 90 pct for the oxidation-carburization, at the expense of higher Cr in the metal; the retention of W and Mo in the metal was significantly higher.

Other elements were not considered to be as pertinent and therefore were not included in the analyses. Included in

TABLE 4. - Distribution of elements in melt-refined alloy ingot and slag, percent

Melt refining[1]	Ni	Co	Cr	Fe	Mo	W
MO:						
Ingot	86	65	~1	26	50	~1
Slag	14	35	99	74	50	99
MO + C:						
Ingot	97	94	13	74	97	79
Slag	3	6	87	26	3	21

[1]MO is melt-oxidized; 135 pct stoichiometric O as roasted sludge. MO + C is oxidized plus carburized; 135 pct stoichiometric O as roasted sludge plus 300 pct stoichiometric C addition (as coke breeze).

the other elements were small amounts of Ti and Al, which oxidize readily and are difficult to reduce; these report to the slag. The slagging additions of CaO, SiO_2, and CaF_2 along with the Al_2O_3 in the grinding sludge make up the major portion of the slag.

The slag was reserved for subsequent slag reduction experiments to produce an Fe-Cr alloy (containing minor amounts of Ni, Co, W, and Mo). Prior research (2-3) indicated that such reduction is technically feasible. Experiments are being conducted in the ongoing research; details will be given in a forthcoming report. For energy conservation in industrial practice, the slag would be removed while hot for the reduction treatment.

CONTROLLED-POTENTIAL ELECTROLYSIS TO DEPOSIT Ni-Co ALLOY

In theory, the controlled-potential mode of electrolysis has the advantage of selective deposition of all elements having a more noble deposition potential than the potentiostat cathode potential setting. Also, those elements with a more negative deposition potential than the value set should be rejected from depositing. However, owing to polarization and related effects, the standard reduction potential sequences are not usually followed, and anomalous effects commonly occur during alloy deposition. Even though these problems occur for multicomponent systems, controlled potential does hold promise for better selectivity and improved deposition over the conventional constant-current method. The cathode potential control can also change behavior of the anode dissolution and valences of dissolved metal species (7); for example, trivalent Cr forms as the dissolving species, whereas hexavalent Cr may form with constant-current conventional cell operation (5). In the past, with few exceptions, controlled potential has been used primarily in analytical procedures and not in prospective metal recycling schemes.

Initial controlled-potential electrolysis on Ni-Co-Cr alloy anode (7) indicated that Ni-Co alloy deposition began (slow rate) at a cathode potential of about -0.6 V versus standard calomel electrode (SCE). Therefore, most of the electrolysis experiments were conducted at -0.75 or -0.90 V versus SCE. Earlier experiments also indicated that electrolyte pH control was critical to attaining good deposits, so most deposition experiments were conducted with the electrolyte pH appropriately controlled by the periodic addition of acid mixtures having the same SO_4-Cl ratio as the electrolyte being used. The acid additions were sometimes made manually, but for most of the experiments, the addition was controlled by a datalogger which triggered a relay to start and stop a peristaltic pump at preset pH values.

The performance of Nafion 425 was assessed as to whether a CSM would help control the transmittal of impurities that tend to codeposit with the Ni-Co alloy.

Experiments were conducted on Ni-Co-bearing electrolytes and soluble anodes which contained only Ni and Co, with the electrolyte doped with either Fe or Cr ions. These experiments were designed to show the effects of soluble Fe or Cr on the codeposition of Ni-Co alloy, while varying parameters such as impurity concentration, impurity valence state, cathode potential, temperature, and use of CSM.

Finally, electrolysis was conducted on soluble melt-refined SA anodes prepared by both the oxidation and the oxidation-plus-carburization procedures.

Effects of Cr

Controlled-potential electrolysis experiments were conducted in a 1-L open cell (no CSM) using 70 Ni-30 Co anode material to determine the tolerance limits for Cr^{3+} ions in acid sulfate-chloride electrolytes over the pH range of 1.0 to 2.0. These 8-h tests were run with the cathode potential controlled at -0.90 V versus SCE. The electrolytes initially contained the usual amounts of divalent Co and Ni, 6.5 and 45 g/L, respectively, with additions of 1 to 60 g/L Cr^{3+}. The pH was maintained at 1.0, 1.5,

or 2.0 during the tests. The ratio of SO_4 to Cl in these electrolytes was approximately 1.

Results of these experiments are shown in table 5 and figure 3. The tolerable amounts of Cr were greatly dependent upon the pH of the electrolyte. At pH 1.0, up to 56 g/L Cr^{3+} could be tolerated with <0.1 pct Cr codeposited with the Ni-Co alloy. However, as the amount of Cr^{3+} was increased, the cathode current efficiency (CE) decreased. At the 56 g/L Cr^{3+} level, the CE had dropped to only 40 pct. The current density (CD) decreased as a function of increasing Cr content and increased pH. At pH 1.5, between 3 and 8 g/L Cr^{3+} was tolerable, and at pH 2.0, <0.3 g/L Cr^{3+} could be tolerated before 0.1 pct Cr was codeposited. A nonmetallic coating, thought to be $Cr(OH)_3$, formed on the cathode, making it difficult to accurately calculate the cathode CE. It is postulated that, as the pH of the electrolyte increased next to the cathode, the nonmetallic coating formed.

Results of previous research (7) had indicated that, at pH 1.2, only about 1 g/L Cr^{6+} could be tolerated in open-cell electrolysis before a drastic reduction in both cathode CE and CD occurred. Additional experiments have been conducted at pH 1.2 using a CSM to separate the catholyte from the anolyte. In these experiments, also using a binary Ni-Co anode, both the catholyte and anolyte contained Co and Ni ions, but Cr ions were added only to the anolyte. Results of these 6-h tests (table 6) showed that, at pH 1.2, 5 g/L Cr^{6+} did not result in codeposition of Cr with Ni-Co as did 5 g/L Cr^{3+}. After deposition, the catholytes analyzed 0.10 and 0.87 g/L Cr, respectively, indicating that Cr^{6+}, when present, is restricted from transferring through the CSM. For the doping with Cr^{6+}, the relatively small amount of Cr entering the catholyte evidently is transmitted as Cr^{3+} reduced from Cr^{6+}. The 5 g/L Cr^{6+} has a more pronounced effect on cathode CD and the deposit Ni-Co ratio than does Cr^{3+}.

TABLE 5. - Effects of Cr^{3+} concentration and pH on cathode current efficiency and Cr codeposition with Ni-Co alloy[1]

Cr^{3+} conc, g/L	Cathode current efficiency, pct	Cr in Ni-Co deposit, pct
AT pH 1.0		
5	69	0.06
10.4	63	.05
20	49	.06
36.5	47	.04
56	40	.01
AT pH 1.5		
0.7	86	0.09
3.3	76	.09
8.1	47	1.1
20.8	ND	11.9
AT pH 2.0		
0.3	95	0.19
.8	ND	3.1
4.0	ND	10.3

ND Not determined.

[1]Ni-Co alloy anode; electrolyte SO_4-Cl ratio ~1; initially 45 g/L Ni and 6.5 g/L Co in electrolyte; open cell (no CSM); Ti cathode.

Effects of Fe

Other controlled-potential electrolytic experiments were conducted in an open cell to decrease the codeposition of Fe with Ni-Co. Increasing the cell temperature from the usual 55° to 85° C caused

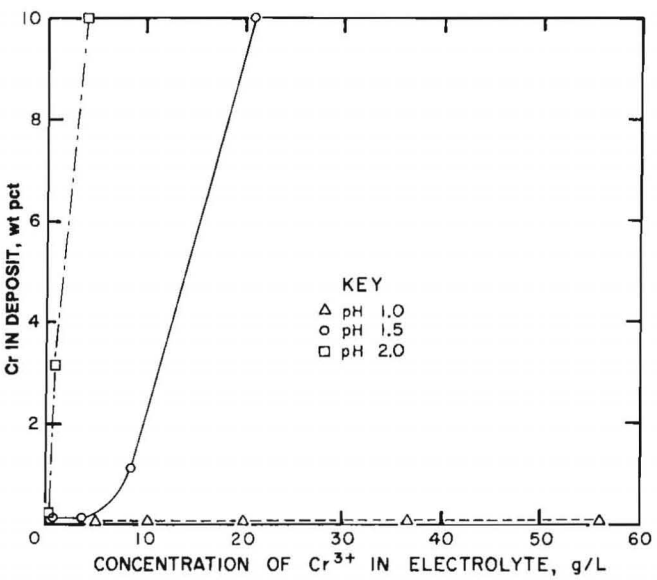

FIGURE 3.—Effect of electrolyte pH on Cr deposition at various concentrations of Cr^{3+} in sulfate-chloride electrolyte.

TABLE 6. - Controlled-potential electrolytic experiments at pH 1.2 in membrane cell with Cr additions

Cr addition, g/L	Cathode data		Chemical analysis					
	CD, A/ft^2	CE, pct	Spent anolyte, g/L			Deposit, wt pct		
			Cr^{6+}	Cr^{3+}	Total Cr	Cr	Co	Ni
Cr^{6+}:								
1.....	43	74	0.3	0.6	0.9	ND	20.1	79.9
5.....	24	67	3.7	.7	4.4	ND	32.6	67.3
Cr^{3+}:								
1.....	57	84	NA	NA	1.1	0.01	18.3	80.6
5.....	45	66	ND	5.6	5.6	.35	21.8	77.7

NA Not available. ND Not detected.

a decrease in the overpotentials, which shifted the Fe deposition potential in the less noble direction. This caused the Fe deposition potential to fall more in line with the standard reduction potentials. Tests were made at lower cathode potential settings of -0.55, -0.60, and -0.70 V versus SCE at cell temperatures of 55° and 85° C. Using electrolytes having an SO_4-Cl ratio of ~1 and doped with 5 g/L Fe^{2+} at a pH of 1.2, and with a cathode potential of -0.55 V versus SCE, 0.7 wt pct Fe was codeposited at 85° C versus 12.4 wt pct at 55° C and -0.70 V versus SCE. These data are shown graphically in figure 4. However, changing the cathode potential in the positive direction caused a substantial decrease in the cathode CD. The effect of the SO_4-Cl ratio in the electrolyte also was determined relative to iron in the deposit. These tests were conducted on electrolytes that were all chloride (68 g/L Cl) or had SO_4-Cl ratios of 0.1, 0.9, and 4.8 at two cathode potentials, -0.65 or -0.90 V versus SCE. The electrolytes contained 5 g/L Fe^{2+}, 6.5 g/L Co, and 45 g/L Ni. Tests at -0.65 V versus SCE potential (also low CD, <10 A/ft^2) indicated that less iron codeposited as the SO_4-Cl was increased (more sulfate). However, the reverse trend was indicated at cathode potentials of -0.90 V versus SCE (CD >50 A/ft^2), where the lowest percentage of iron in the deposit occurred in the all-chloride electrolyte (fig. 5).

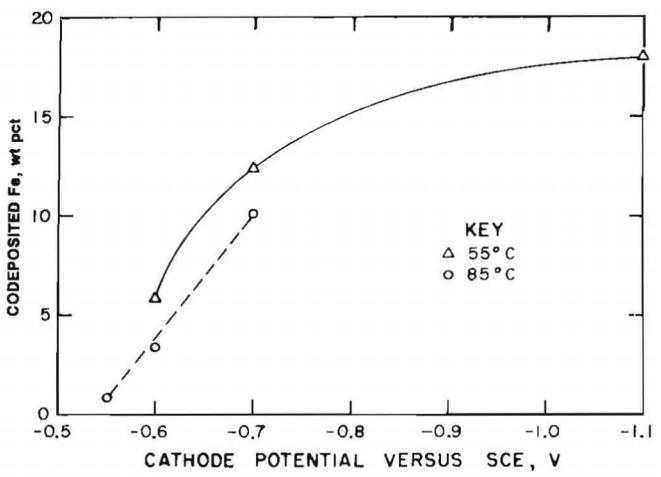

FIGURE 4.—Effects of cell temperature and cathode potential on Fe codeposition with Ni-Co.

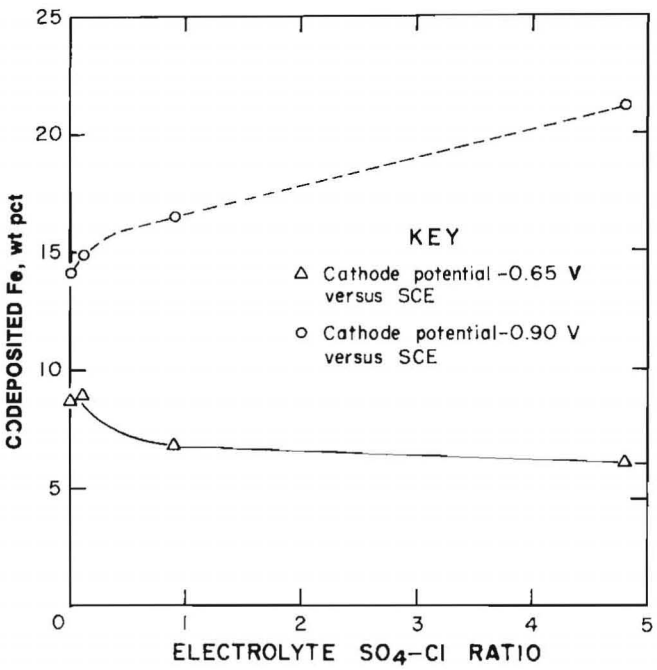

FIGURE 5.—Relationship of SO_4-Cl ratio in electrolyte to Fe codeposition at cathode potentials of -0.65 and -0.90 V versus SCE

Electrolytic experiments were conducted using a CSM (Nafion 425) to separate the catholyte from the anolyte cell compartments to determine the effect on iron codeposition with the Ni-Co alloy (SO_4-Cl ratio ~1). Tests in which the anolyte was doped with 5 g/L Fe^{2+} showed that about 3.9 pct Fe was deposited with the Ni-Co alloy versus about 16 pct Fe without using a membrane. Similarly, tests in which the anolyte contained 5 g/L Fe^{3+} resulted in 1.5 pct Fe in the deposit when the CSM was used versus 18 pct Fe without the CSM. A few tests were conducted with the anolyte containing high chloride (~200 g/L Cl) and 5 g/L Fe^{3+}. After 8 h in the membrane cell, about 0.9 pct Fe was codeposited.

A few additional experiments were made, without much success, in the CSM cell to try to complex iron and thus decrease its codeposition. These included the addition of HF, citric acid, salicylic acid, or pyridine to the anolyte, which contained 5 g/L Fe^{2+} or Fe^{3+}. Other ongoing research directed toward decreasing codeposition of Fe with the Ni-Co includes experiments to precipitate Fe by pH increase and oxidation during periodic treatment or continuous bleeding of the electrolyte for purification.

Electrorefining Superalloy Scrap Anodes

Controlled-potential electrolysis experiments were conducted on melt-oxidation-refined SA scrap, utilizing such variables as electrolyte temperature, composition, and pH, and controlled-potential setting, which had been indicated as desirable in the previous work (7). The anode composition was, in wt pct, 76.0 Ni, 19.0 Co, 0.11 Cr, 1.33 Fe, 2.5 Mo, <0.05 W, and <0.05 C. The distribution of elements between the slag and metal was that given in table 4. The results of a 24-h electrorefining experiment will be given to illustrate the behavior. For this experiment, two melt-oxidized scrap anodes (about 250 g each) and one stainless steel (316) cathode (1.5 by 6 by 0.035 in) were spaced 1.5 in apart. Nafion 425 membrane separated the anolyte (1,025 mL) from the catholyte (375 mL). The electrolyte temperature was 55°±1° C, and the pH of both anolyte and catholyte was controlled at 1.0 by the addition of 99.5 vol pct concentrated HCl plus 0.5 vol pct concentrated H_2SO_4. The cathode potential was controlled at -0.90 V versus SCE. The starting high-chloride electrolyte, both anolyte and catholyte, had the following composition:

62 g/L Cl (HCl + Ni,Co chlorides)

2 g/L SO_4 (added as H_2SO_4)

45 g/L Ni

6.5 g/L Co

Pertinent cell operation data for the experiment are given in table 7.

Some of the more pertinent data are that there was 0.77 g/(A•h) cathode deposit and 1.12 g/(A•h) anode dissolution; this translates to 1.85 kW•h of electrical energy per kilogram of cathode deposit (98.9 pct Ni + Co). The anode CE was 99 pct, and the cathode CE was 71 pct.

Compositions of the deposit and anode sludge are given in table 8. The material balance distributions of Ni and Co are given in table 9, and those of Cr, Fe, and Mo are given in table 10 for the melt-oxidized electrorefined scrap.

Ideally, the deposit should have the same Ni-Co ratio as that present in the anode for sustained operation. Residual anode and electrolyte analyses have confirmed that dissolution is generally

TABLE 7. - Cell operation data in 24-h test using melt-oxidized superalloy scrap anodes

Anode dissolved	g	94.7
Cathode deposit	g	64.8
Anode sludge formed	g	1.84
Anode current efficiency	pct	99
Cathode current efficiency	pct	71
Cathode current density	A/ft^2	40
Average cell voltage	V	1.43
Total cell power	A•h	84.17
Anode dissolution	g/(A•h)	1.12
Ni-Co alloy deposit	g/(A•h)	0.77
Electrical energy consumed	kW•h	0.120
Energy per kg of Ni-Co deposit	kW•h	1.85

uniform with no selective enrichment or depletion of Ni, Co, Cr, or other elements in the undissolved anode (exclusive of anode sludge). In this experiment, a slightly higher ratio of Ni-Co was deposited (tables 8-9) relative to the ratio in the anodes. The fact that experiments indicate that Co deposits somewhat more readily than Ni and apparently migrates somewhat more slowly through the membrane than Ni when at lower concentrations tends to add to the difference in deposition ratios. Transference of ions through the membrane appears to be dependent on ionic concentration. With the cell configuration used, the transference of Ni and Co cations through the membrane was not as rapid as the deposition rate; there was, therefore, some buildup of Ni and Co ions in the anolyte while the catholyte was being depleted of these ions during deposition. There are several possible ways to compensate for this situation, such as increasing the relative membrane area, using a thinner membrane, increasing the relative catholyte volume, or circuiting purified anolyte to the catholyte chamber to help maintain the Ni and Co ion concentration. Such aspects are the subject of ongoing research.

Electrolysis data for the melt-oxidized anode material show that very little insoluble Cr, Fe, and Mo were present, as indicated by the small amount of anode sludge formed (tables 7 and 10). Only about 6 pct of the Mo present in the anode reported to the anode sludge, and <2 pct of both the Cr and Fe present remained as sludge.

The deposition of Mo was restricted primarily because of the restricted transport of the Mo ions through the membrane. The final anolyte contained >1 g/L Mo, yet the deposit contained <0.01 wt pct Mo.

Under the conditions employed, melt-oxidation refining of the SA scrap to

TABLE 8. - Deposit and anode sludge analyses (partial) when using melt-oxidized anodes,[1] weight percent

	Deposit	Anode sludge
Ni	79.8	55.4
Co	19.1	12.9
Cr	.02	.07
Fe	.62	1.31
Mo	<.01	7.57

[1]24-h test.

TABLE 9. - Material balance for Ni and Co in electrolysis when using melt-oxidized anodes[1]

	Grams			Distribution of Ni + Co, pct
	Ni	Co	Ni + Co	
Dissolved in solution:				
Dissolved-nondeposited	20.6	5.7	26.3	28.7
Deposited	51.7	12.4	64.1	70.0
Total	72.3	18.1	90.4	98.7
In anode sludge	1.0	.2	1.2	1.3

[1]24-h test.

TABLE 10. - Material balance for Cr, Fe, and Mo in electrolysis when using melt-oxidized anodes[1]

	Grams			Distribution of Cr + Fe + Mo, pct
	Cr	Fe	Mo	
Dissolved in solution:				
Dissolved-nondeposited	0.10	0.86	2.3	85.1
Deposited	.01	.40	<.01	10.7
Total	.11	1.26	2.3	95.8
In anode sludge	.001	.02	.14	4.2

[1]24-h test.

form anode material (without subsequent melt-carburizing) has both advantages and disadvantages. Advantages are--

1. Removes >99 pct of the Cr to slag phase.
2. Decreases other soluble impurities such as Fe, Mo, and W in the anode material.
3. Increases the grade of Ni + Co in the anode material.
4. Deposited Ni-Co alloy contains <1 pct impurities.
5. Increases time of deposition before electrolyte purification is necessary.

Disadvantages are--

1. Results in large losses to the slag: ~35 pct of Co, 15 pct of Ni, 50 pct of Mo, and 99 pct of W.
2. High overall recovery of Ni + Co would require separation from the slag.
3. Cannot remove Cr, Mo, and W as anode sludge carbides.

Electrorefining experiments also were conducted using controlled-potential electrolysis on melt-oxidized-carburized SA scrap anode material. Using the previously described melt-refining procedure for sequential oxidation and carburizing, a much higher proportion of the Ni + Co was retained as metal for anode preparation. Distribution of the six most pertinent elements was that given in table 4. The composition of the oxidized-carburized anode material was, in wt pct, 58.5 Ni, 18.5 Co, 5.4 Cr, 8.7 Fe, 3.6 Mo, 3.5 W, and 1.2 C.

For the melt-oxidized-carburized anode material, the 2-L electrolytic cell with two anodes and one stainless steel cathode was operated with the same electrolyte and under the same conditions as previously described for the melt-oxidized anodes. This test was conducted for a longer time period of 70.5 h with a new cathode put into service after each 24-h period. The cell operation data for the experiment using the melt-oxidized-carburized anode material are given in table 11. Compared to the melt-oxidized anodes (tables 7), somewhat less anode dissolved per ampere hour for the oxidized-carburized anodes, but the amount of cathode deposit per ampere hour was only slightly less. The calculated energy consumed per kilogram of Ni-Co deposit was 2.34 kW·h, some 26 pct more than for the melt-oxidized anodes. This is reflected in the somewhat lower values realized for the CE for both the anode and cathode, attributed mainly to the substantially increased presence of Cr in solutions.

TABLE 11. - Cell operation data for 70.5-h experiment using melt-oxidized-carburized superalloy scrap anodes

Anode dissolved	g	279.0
Cathode deposit	g	209.7
Anode sludge formed	g	37.7
Anode current efficiency	pct	91
Cathode current efficiency	pct	69
Cathode current density	A/ft^2	42
Average cell voltage	V	1.77
Total cell voltage	A·h	278.59
Anode dissolution	g/(A·h)	1.00
Ni-Co alloy deposit	g/(A·h)	0.75
Electrical energy consumed	kW·h	0.49
Energy per kg of Ni-Co deposit	kW·h	2.34

There was no evidence of anode passivation. Dissolution remained efficient and uniform throughout the electrolysis period although significant quantities of porous anode sludge were formed. In fact, there was no indication of anode passivity for any of the melt-oxidized or oxidized-carburized scrap anodes. Good anode dissolution is attributed in part to the higher chloride than sulfate content of the electrolyte--prior research (7) indicated apparent passivity with all-sulfate electrolyte--and in part to the use of controlled potential, which also limits the anode potential to less oxidizing conditions. This is reflected in the consistent dissolution of Fe and Cr as the lower-oxidation-state Fe^{2+} and Cr^{3+} ions.

Compositions of the deposit and anode sludge are given in table 12. The deposit from the oxidized-carburized anodes had a substantially higher Ni-Co ratio than that present in the anodes. Previous research (7) had shown that factors such as electrolyte SO_4-Cl ratio and controlled-potential setting affect the Ni-Co ratio of the deposit. The inclusion

of a CSM is an additional factor affecting deposit Ni-Co ratio. The influence of the deposit Ni-Co ratio relative to that of the anode material is under continuing evaluation for longer term depositions. Included are aspects such as anolyte purification and recircuiting to the catholyte and starting with an electrolyte Ni-Co ratio more nearly the ratio of the anode material. The anode sludge for the oxidized-carburized anodes contained a much lower weight percentage of Ni, Co, and Fe than the melt-oxidized anode material (table 8) and significantly more Cr, W, Mo, and C. This reflects the presence of insoluble carbides of Cr, W, and Mo resulting from the melt-carburization subsequent to the melt-oxidation. The anode sludge has been confirmed by X-ray diffraction to contain Mo_2C and tentatively WC_{1-x} and Cr_2C.

The material balance and distribution of Ni and Co during electrolysis are shown in the data given in table 13. Some 56.6 pct of the Ni + Co available in the anode was dissolved into the electrolyte, and 1.2 pct of the Ni + Co remained as anode sludge. Considering only the Ni + Co solubilized, the Ni + Co in the anode sludge, and the Ni + Co remaining in the electrolyte (gain over starting electrolyte), roughly 2 pct of the Ni + Co remained as anode sludge, somewhat over 85 pct deposited, and the balance remained as dissolved Ni + Co in the electrolyte (available for deposition with sustained operation).

The data for the material balance and distribution of Cr, Fe, W, and Mo in the electrolysis (table 14) confirm that a considerable portion of these elements (~29 pct in this test) is tied up as insoluble carbides (mainly Cr, W, and Mo) in the anode material from the melt carburization. Of the approximately 71 pct of these elements solubilized, only 9 pct reports to the deposit, mainly as Fe. Apparently, most of the Fe migrates through the membrane as Fe^{2+}. Cursory tests indicate that if the Fe could be oxidized to and maintained as Fe^{3+} in the anolyte, a reduction in the codeposition of Fe probably would occur. Ferric iron could also be readily precipitated to purify the electrolyte by raising the pH. Solubilized W and Mo are, to a large extent, restricted from passing through the membrane and remain in the anolyte. Ongoing experiments confirm that periodically or continuously bled electrolytes can be purified by raising the pH and precipitating Fe^{3+} and Cr^{3+} with relatively small losses of Co and Ni. Tungsten and molybdenum coprecipitate. The precipitate is rich in Fe and Cr and could revert to the slag carbothermic reduction treatment, or to other outlets.

TABLE 12. - Deposit and anode sludge analyses (partial) when using melt-oxidized-carburized anodes,[1] weight percent

	Deposit	Anode sludge
Ni	81.2	11.6
Co	16.0	1.9
Cr	.10	10.6
Fe	2.73	.7
Mo	<.01	16.2
W	<.01	23.6
C	ND	9.2

ND Not determined. [1]70.5-h test.

TABLE 13. - Ni and Co material balance in electrolysis when using melt-oxidized-carburized anodes[1]

	Grams			Distribution of Ni + Co, pct
	Ni	Co	Ni + Co	
Dissolved in solution:				
Dissolved-nondeposited	6.1	22.9	29.0	12.2
Deposited	170.1	33.5	203.6	85.7
Total	176.2	56.4	232.6	97.9
In anode sludge	4.4	.7	5.1	2.1

[1]70.5-h test.

TABLE 14. - Material balance for Cr, Fe, Mo, and W in electrolysis when using melt-oxidized-carburized anodes[1]

	Grams				Distribution of Cr + Fe + Mo + W, pct
	Cr	Fe	Mo	W	
Dissolved in solution:					
Dissolved-nondeposited.....	12.5	20.9	5.0	1.9	61.5
Deposited.....	~.2	5.7	<.03	<.03	9.0
Total.....	12.7	26.6	5.0	1.9	70.5
In anode sludge.....	4.0	.3	6.1	8.9	29.5

[1]70.5-h test.

TABLE 15. - Overall distribution of metals in slag, anode sludge, deposit, and electrolyte for melt-oxidized versus oxidized-carburized superalloy scrap, perecnt

Distribution[1]	Ni	Co	Cr	Fe	Mo	W
Refining: Slag						
MO.....	14	35	99	74	50	99
MO + C.....	3	6	87	26	3	21
Electrolytic:						
Anode sludge:						
MO.....	1	1	<.01	<.5	2	NA
MO + C.....	2	1	3	<1	53	65
Deposit:[2]						
MO.....	61	44	<.1	8	<.2	NA
MO + C.....	92	55	<.2	16	<.2	<.2
Dissolved--nondeposited:						
MO.....	24	20	~1	17.5	48	NA
MO + C.....	3	38	10	57	44	~14

NA Not available.

[1]MO is melt-oxidized; 135 pct stoichiometric O as roasted sludge. MO + C is oxidized plus carburized; 135 stoichiometric O as roasted sludge plus 300 pct stoichiometric C addition (as coke breeze).

[2]For melt-oxidized (MO), deposition period 24 h; for oxidized plus carburized (MO + C), deposition period 70.5 h.

The solubilized Cr is closely watched. It dissolves as the Cr^{3+} species. Without oxidation, it passes relatively readily through the membrane as Cr^{3+}. If it reaches high enough values in the catholyte, cathode CE can be decreased significantly. However, the removal of most of the Cr in the melting restricts its access to the cell. In the cell, about one-fourth of the Cr in the anode is tied up as insoluble carbidic anode sludge. The controlled-potential mode with pH control affords a means to tolerate considerable Cr in the system while maintaining acceptable Ni-Co deposition behavior. Sustained longer term cell operation would still require some Cr purification of the electrolyte.

A comparison of the overall recoveries or product distributions of metals from SA scrap can be made from the data obtained using anodes prepared by melt-oxidation versus those that had been oxidized-carburized. These percentage recoveries and distributions are shown in table 15. It should be realized that the Ni + Co left in the electrolyte in both instances is recoverable as Ni-Co deposit with sustained operation. Well over 90 pct of the total Ni + Co can be recovered electrolytically from the oxidized-carburized anode, as shown in table 15.

The main difference in Ni + Co recoverable for the two melt-refining schemes is the much larger proportion partitioned to the slag with melt-oxidation only. Similarly, most of the W and Mo are delegated to the slag with melt-oxidation only, whereas with oxidation-carburization, the major portion of these metals will report as recoverable anode sludge.

Figure 6 shows a simplified flow diagram for recovery of the Ni, Co, Cr, and other critical metals from mixed and contaminated SA scrap.

SUMMARY AND CONCLUSIONS

This report is an intermediate progress report discussing partial results of ongoing research to recover Ni, Co, and other critical metals from mixed and contaminated superalloy scrap. The approach involves pyrometallurgical melt refining to produce anode material suitable for electrometallurgical recovery of Ni-Co alloy codeposited using a controlled-potential mode of cell operation in the electrorefining. The following summations and conclusions can be made relative to the current research status.

Mixed contaminated superalloy scrap can be melt-oxidized to partition >95 pct of the Cr to the slag along with the

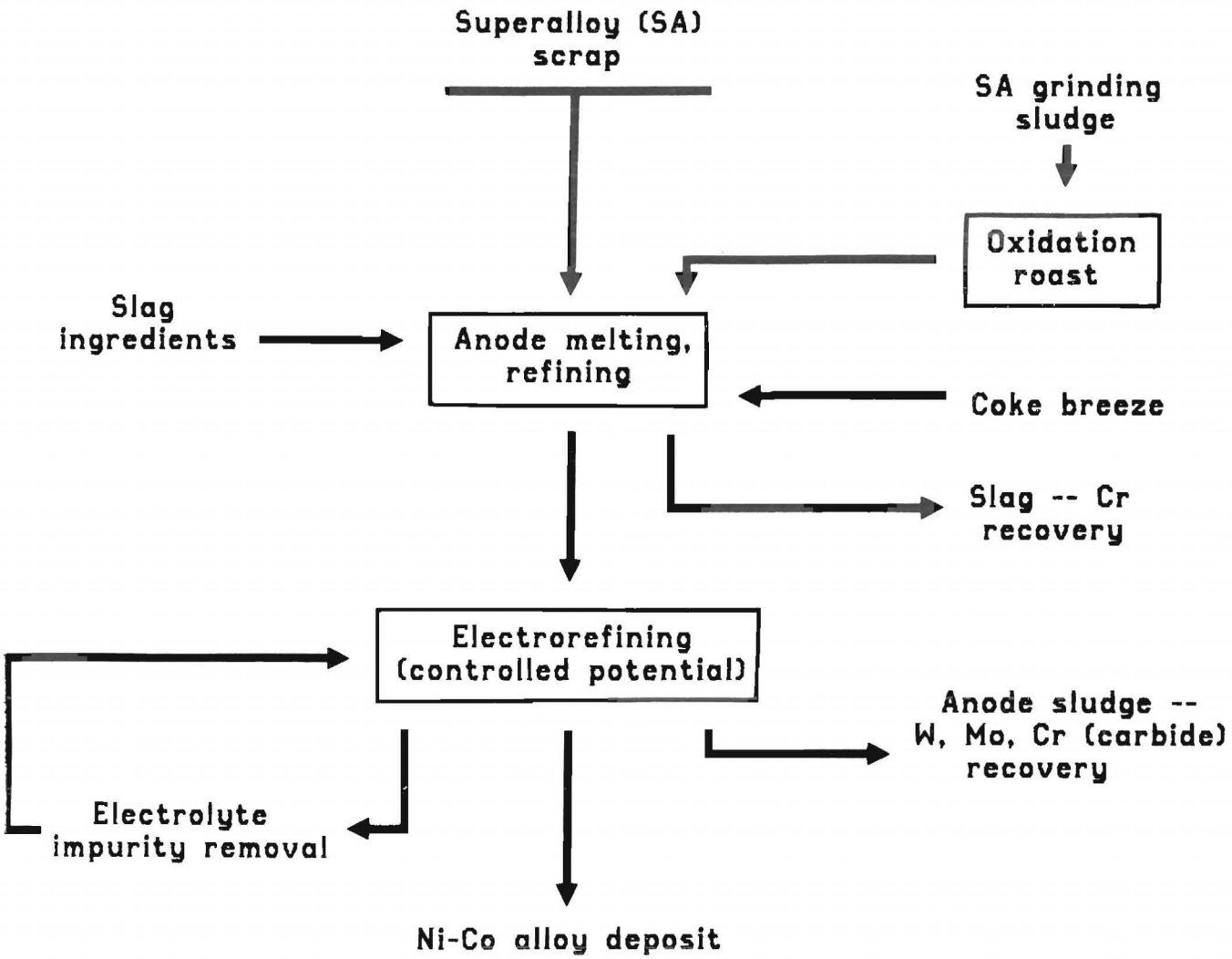

FIGURE 6.—Simplified flow diagram for recovery of Ni, Co, Cr, and other values from mixed contaminated superalloy scrap.

majority of the contained W, Mo, and Fe, using roast-oxidized superalloy grinding sludge to provide the O source. Most of the Ni and Co contained in both the superalloy bulk scrap and the oxidized superalloy sludge will report to the metal phase, which is cast into anodes; however, there is substantial loss of Ni and Co to the slag when high proportions of Cr are oxidized to the slag under the conditions used.

Subsequent controlled carburization of the melt after melt-oxidation is effective in significantly increasing the proportion of Ni and Co reporting to the metal phase, to some 95 pct, although some 10 to 20 pct of the Cr will simultaneously reduce to the metal phase. The carburization also has the advantage of partitioning the majority of the contained W and Mo to the metal phase as carbides, which, along with some Cr (and other carbide formers, if present), remain as insoluble anode sludge for recovery by subsequent processing.

Electrolysis of superalloy scrap anodes, with anolyte and catholyte compartments separated with a cationic selective membrane (CSM), can produce codeposited Ni-Co alloy when operating with a controlled-potential mode using acidic chloride-sulfate electrolyte.

The acidic chloride-sulfate electrolyte readily dissolves superalloy scrap; anode dissolution is not a limiting factor. Electrolytes with relatively high chloride contents perform better overall from the standpoint of dissolution rate and cathode current efficiency.

The controlled-potential mode of cell operation, when maintained at proper potential for Ni-Co deposition, has the advantage, particularly in conjunction with use of a CSM, of restricting deposition of impurity elements. The controlled potential also affects the extent of oxidation of dissolving metal ions, characteristically leaving them in lower oxidation states, which aids cathode current efficiency.

For superalloy scrap anodes refined by sequential melt-oxidation and melt-carburization, approximately three-fourths of the residual Cr will dissolve in the electrolyte, with the remainder reporting as carbidic anode sludge. Hexavalent chromium (Cr^{6+}) does not migrate through the CSM as readily as does Cr^{3+}. However, for the experimental conditions employed thus far, the Cr dissolves as Cr^{3+} rather than as Cr^{6+}. When using a Nafion 425 CSM, Cr^{3+} will migrate somewhat from the anolyte to the catholyte, where it can reduce current efficiency (CE) when present at more than about 5 g/L at pH 1.5. The effect of Cr^{3+} on CE is very pH dependent, being much less at low pH. It is, therefore, beneficial to operate at lower pH, although CE for Ni-Co deposition in general decreases with decreased pH.

Iron is an impurity commonly present in mixed contaminated superalloy scrap. A number of superalloys have some Fe content. Although some Fe can be removed in melt-refining, nowhere near quantitative removal can be achieved with the procedures used without excessive loss of Ni and Co. In the cell, Fe readily codeposits with Ni-Co (anomalous to idealized standard reduction potentials). Some Fe can be tolerated in a Ni-Co master alloy, but the usefulness would be improved if Fe could be restricted from codeposition. This was not achieved in the current work, but is the subject of ongoing research.

Codeposits of Ni-Co alloy containing >97 pct Ni plus Co can be readily produced by controlled-potential electrolytic refining of melt-refined superalloy scrap anodes, with the main impurities being Fe and Cr. Small amounts of Cr are not in themselves detrimental to a Ni-Co master alloy. The presence of Cr in the deposit to any substantial extent, however, indicates disminishing CE and impending problems. Buildup of Cr in the electrolyte will require some electrolyte purification. Small amounts of soluble

W and Mo, in addition to amounts formed as anode sludge, also would be removed in electrolyte purification. Tungsten and molybdenum did not pass the CSM, and the small dissolved amounts appeared essentially only in the anolyte. Electrolyte purification is a topic of continuing research, as is longer term Ni-Co deposition.

The anode sludge formed from melt-oxidized-carburized anodes has been characterized as consisting mainly of W, Mo, and Cr carbides with some entrained amounts of Ni, Co, Fe, etc. If not separable to distinct carbides, such material might be directly reusable in tool steels or other special alloys where the benefit of the critical metals would be realized. Preliminary experiments indicate that the slags formed in melt refining can be reduced to produce an Fe-Cr alloy for use in steelmaking. These areas of metal recovery are also the subject of ongoing research.

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